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Cleaning Nanoelectrodes with Air Plasma

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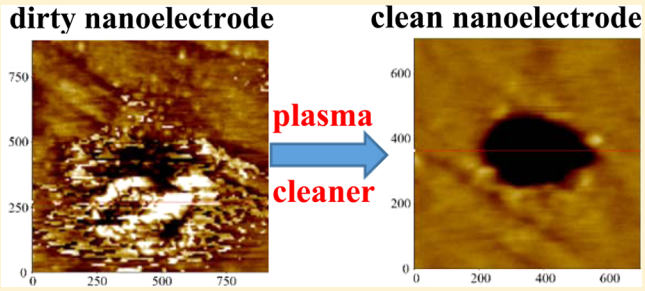
ABSTRACT: Unlike macroscopic and micrometer-sized solid electrodes whose surface can be reproducibly cleaned by mechanical polishing, cleaning the nanoelectrode surface is challenging because of its small size and extreme fragility. Even very gentle polishing typically changes the nanoelectrode size and geometry, thus, complicating the replication of nanoelectrochemical experiments. In this letter, we show the possibility of cleaning nanoelectrode surfaces nondestructively by using an air plasma cleaner. The effects of plasma cleaning have been investigated by atomic force microscopy (AFM) imaging, voltammetry, and scanning electrochemical microscopy (SECM). A related issue, the removal of an insoluble organic film from the nanoelectrode by plasma cleaning, is also discussed.



The development and applications of nanometer-sized electrodes have been the subject of numerous research publications during the last 2 decades.[1] Nanoelectrodes offer important advantages and enable investigations of various phenomena and processes that cannot be studied at macroscopic electrodes.[2] These include electrochemistry of single molecules and nanoparticles,[3] formation and growth of individual metal nuclei[4] and nanobubbles,[5] rapid heterogeneous electron transfer kinetics,[6] and electrochemistry inside living cells.[7] The availability of nanoelectrode tips greatly improved spatial resolution of the scanning electrochemical microscopy (SECM).[8] At the same time, handling nanoelectrodes can be surprisingly difficult. For example, the Amemiya group recently showed that major damage to a glass-sealed metal nanoelectrode can be caused just by touching it without proper protection against the electrostatic discharge.[9] Another tricky issue is cleaning the nanoelectrode surface, which often gets contaminated by impurities present either in solution or in the laboratory air. The conductive surface of a nanoelectrode is easily covered because of its tiny area and very fast mass transport at the nanoscale, and the presence of organic impurities can affect the rates and mechanisms of electrocatalytic reactions.[10] While cleaning a micrometer-sized or larger electrode by mechanical polishing is relatively straightforward, for a nanoelectrode this procedure is likely to change the effective radius (a) and shape of the conductive surface as well as RG (RG = r_g/a, where r_g is the radius of the insulating glass sheath) and can make it unsuitable for further experiments. An alternative approach, to clean the electrode by immersion in a piranha solution or organic solvent, is not always effective. The loss of a contaminated nanoelectrode is a problem not only because its preparation is labor-intense but also because fabricating two very similar nanoelectrodes is nearly impossible. Thus, cleaning the electrode surface is essential for reproducibility of nanoelectrochemical experiments.

The gas plasma has been widely used to clean and activate surfaces by removing most organic impurities.[11] In this letter we show the possibility of cleaning nanoelectrodes with gas plasma and discuss its effects on the electrode response and geometry. The initial surface contamination and the effectiveness of cleaning are evaluated by using recently developed methodology for AFM imaging of nanoelectrodes.[12]

A closely related issue is the need to remove an organic film from the nanoelectrode surface. Different kinds of films ranging from molecular monolayers to electronically and ionically conductive polymers to proteins have been formed on electrode surfaces and employed in electrochemical experiments. To reproduce such an experiment, one has to remove the film and restore the electrode surface. Some surface films are easy to remove, e.g., a small amount of Ag electrodeposited on the Pt nanoelectrode could be dissolved anodically without significantly affecting the underlying Pt surface.[4] When the film is hard to dissolve, mechanical polishing and fabricating a new nanoelectrode are the only currently available options if one needs to repeat an experiment. The plasma cleaning can provide a nondestructive means for removing such a film.

■ EXPERIMENTAL SECTION

Chemicals. Ferrocenemethanol (FcMeOH, 97%, Sigma-Aldrich) was sublimed before use. KCl (Sigma-Aldrich), acetonitrile (ACROS), nitrobenzenediazonium tetrafluoroborate, and tetrabutylammonium tetrafluoroborate (Bu_4NBF_4; Alfa Aesar) were used as received. Aqueous solutions were prepared using deionized water with total organic carbon (TOC) ≤ 5 ppb from the Milli-Q Advantage A10 system equipped with Q-Gard T2 Pak and a Quantum TEX cartridge.

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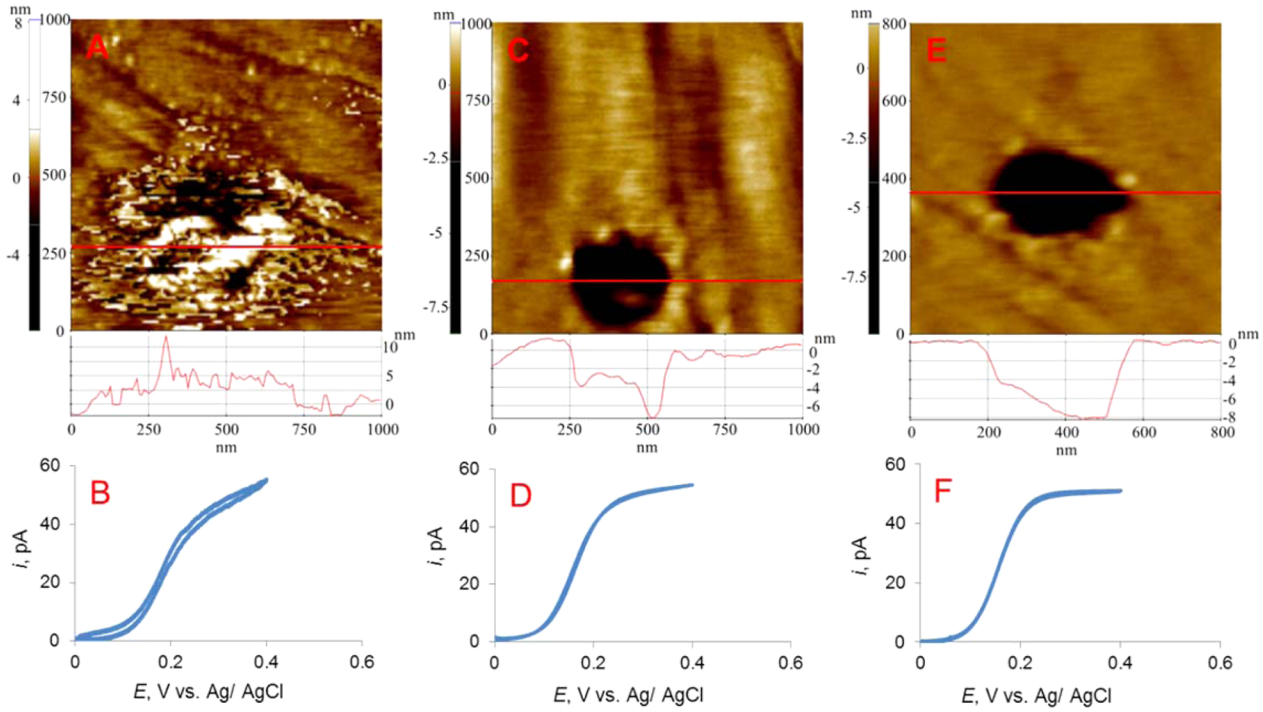

Figure 1. Noncontact topography images of a polished Pt nanoelectrode before (A), after first (C), and second plasma cleaning (E) and corresponding steady-state voltammograms (B, D, and F). The red lines in parts A, C, and E correspond to the shown cross sections. Each cleaning time was 15 min. Solution contained 1 mM FcMeOH and 0.1 M KCl. The potential sweep rate was v = 100 mV/s.

Preparation of Nanoelectrodes. Pt nanoelectrodes were fabricated as described previously.[13a] Briefly, disk-type electrodes were prepared by pulling 25 μm-diameter annealed Pt wires into borosilicate capillaries (Drummond; o.d., 1.0 mm; i.d., 0.2 mm) with the help of a P-2000 laser puller (Sutter Instrument Co.). The pulled nanoelectrodes were polished on a 0.05 μm alumina disk (Precision Surfaces International) under video microscopic control. The electrode radius was evaluated from AFM images and steady-state voltammograms of ferrocenemethanol. The radius varied from 100 to 400 nm and the RG value was between 6 and 15.

A two electrode cell was employed for electrochemical measurements. The nanoelectrode was used as a working electrode and an Ag/AgCl wire served as a reference. Voltammograms were obtained using a BAS 100B electrochemical workstation (Bioanalytical Systems West Lafayette, IN). All experiments were carried out at room temperature (22−25 °C) inside a Faraday cage.

Polymer films were formed on nanoelectrodes in acetonitrile solution containing 5 mM nitrobenzene diazonium tetrafluoroborate and 0.1 M Bu_4NBF_4. The potential was swept from −0.2 V to −1.3 V vs Ag/AgCl with a scan rate of 100 mV/s.

Plasma Cleaning. A PDC-32G plasma cleaner (Harrick plasma) was employed for cleaning nanoelectrodes. First, an electrode was placed inside the chamber of the plasma cleaner and the pump was turned on to create a vacuum of ∼200 mTorr. Then, the metering valve was slightly opened to draw air into the chamber and increase the pressure to 800−1000 mTorr. The gas plasma was generated for 15 min to clean nanoelectrodes and for 30 min to remove an organic film from the electrode surface. After cleaning, a nanoelectrode was removed from the chamber and rinsed with deionized water.

SECM Setup. SECM experiments were carried out using a home-built instrument, which was described previously.[8a] The 100 nm-thick evaporated Au film on glass prepared with the aminosilane coupler and annealed was used as the substrate in positive feedback experiments. To obtain an SECM approach curve, the electrode used as a tip was first positioned a few hundred micrometers above the substrate surface. To avoid crashing, this process was monitored with a long-distance video microscope. Then, the tip was moved closer to the substrate in the automated "surface hunter" mode until the tip current produced by oxidation of FcMeOH increased by ∼10%. The tip current was collected during the subsequent fine approach.

AFM Imaging. An XE-120 scanning probe microscope (Park Systems) and PPP-NCHR probes (Nanosensors) were employed for noncontact imaging of nanoelectrodes in the air. The procedures for nanoelectrode imaging were described previously.[12] Briefly, a nanoelectrode was mounted vertically with its polished surface facing the AFM probe using a homemade sampler holder, and the cantilever was positioned above it with the help of an optical microscope. In a noncontact mode, the tip was brought within a close proximity of the sample using the approach function and then the nanoelectrode was moved laterally in 200 nm steps to bring the AFM probe to its apex. The travel direction was selected to effect z-axis retraction of the piezo actuator in a close-loop mode. This corresponded to sliding of the slanted tip surface along the edge of the glass of the insulating sheath of the nanoelectrode. When the piezo approached its upper limit, the z-stage motor was retracted by 2 μm to maintain the piezo actuator within its range (12 μm).

■ RESULTS AND DISCUSSION

An AFM image of a Pt nanoelectrode after polishing on alumina lapping tape is shown in Figure 1A. The metal surface is not visible because of a thick layer of impurities. The film was sufficiently permeable to FcMeOH to produce a moderately

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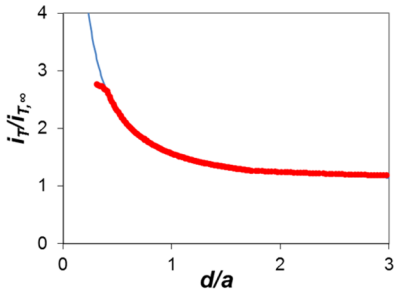

Figure 2. Experimental (red) and theoretical (blue)[15] SEC M approach curves obtained with a nanoelectrode tip after two rounds of plasma cleaning. The current and distance are normalized by $i_{T,\infty}$ = 51 pA and a = 170 nm, respectively. Solution contained 1 mM FcMeOH and 0.1 M KCl.

distorted steady-state voltammogram with only slightly diminished diffusion limiting current (Figure 1B). As discussed previously,[14] the fast, outer-sphere oxidation of FcMeOH is only slightly affected by surface contamination, while major changes could be expected in voltammograms of an inner-sphere reaction.

In an AFM image of the same nanoelectrode obtained after a 15 min treatment in the plasma cleaner (Figure 1C), the Pt surface is clearly visible and the film is gone. The clean surface of glass exhibits subnanometer scale roughness, and the Pt surface is very slightly recessed into the insulator. The recess depth (<7 nm) is negligible in comparison to the electrode radius, $a \approx 170$ nm; it should not produce any appreciable effect on the current.[13b] The electrochemical response of this electrode significantly improved after cleaning. A sigmoidal and essentially retraceable steady-state voltammogram of FcMeOH (Figure 1D) has a much better defined plateau. From the diffusion limiting current, $i_{T,\infty}$ = 51 pA, the effective radius value, a = 170 nm was extracted using eq 1

$$i_{T,\infty} = 4FDca \tag{1}$$

where F is the Faraday constant, $D = 7.8 \times 10^{-6}$ cm^2/s,[13a] and $c = 10^{-6}$ mol/cm^3 are the diffusion coefficient and the bulk concentration of FcMeOH, respectively. The a value is in agreement with that obtained from the AFM image.

A fully retraceable steady-state voltammogram of FcMeOH with a completely flat diffusional plateau (Figure 1F) was obtained after another 15 min of plasma cleaning. The corresponding AFM image (Figure 1E) shows essentially unchanged size and recess depth of Pt and the same low roughness of surrounding glass. These observations along with the unchanged $i_{T,\infty}$ value suggest that neither metal surface nor glass insulator are damaged by the plasma treatment.

After the second round of plasma cleaning, the same nanoelectrode was used as the tip in the scanning electrochemical microscope (SECM). The experimental current vs distance curve obtained with this tip approaching a conductive Au substrate (red line in Figure 2) fits the theory for pure positive feedback (blue curve) very well up to the deviation point at which the surrounding glass touched the substrate surface. The attained maximum feedback current of $2.7i_{T,\infty}$ is not very high because of the relatively large RG = 7.5 and imperfect tip/substrate alignment. However, the a = 170 nm obtained from the fit agrees very well with the radius value found from the diffusion limiting current and AFM images in Figure 1, indicating that the geometry and electrochemical response of the plasma-cleaned tip are suitable for SECM experiments. The advantage of cleaning tips by plasma is significant because polishing typically increases the RG value and, thus, makes the tip less useful as an SECM probe.

The possibility of removing organic film from a nanoelectrode by plasma cleaning is shown in Figure 3. Initially, a ~340 nm-radius Pt electrode was clean and essentially flat (the maximum recess depth was ~16 nm; Figure 3A). To modify the electrode surface, its potential was swept from −0.2 V to −1.3 V vs Ag/AgCl in acetonitrile solution of nitrobenzenediazonium tetrafluoroborate. As expected from the literature,[16] a thick polymer film was electrografted to the electrode surface (Figure 3B). Unlike simple reduction of diazonium salts at bare metal electrodes that typically produces a few nanometer thick insulating multilayer,[17] the reduction of nitrobenzenediazonium occurs at more negative potentials and yields thicker and conductive polymerized films.[16] The ~160 nm-thick film in Figure 3B entirely covers the Pt surface extending beyond its limits to cover a small portion of the glass insulator. After the 30 min treatment in the plasma cleaner, the

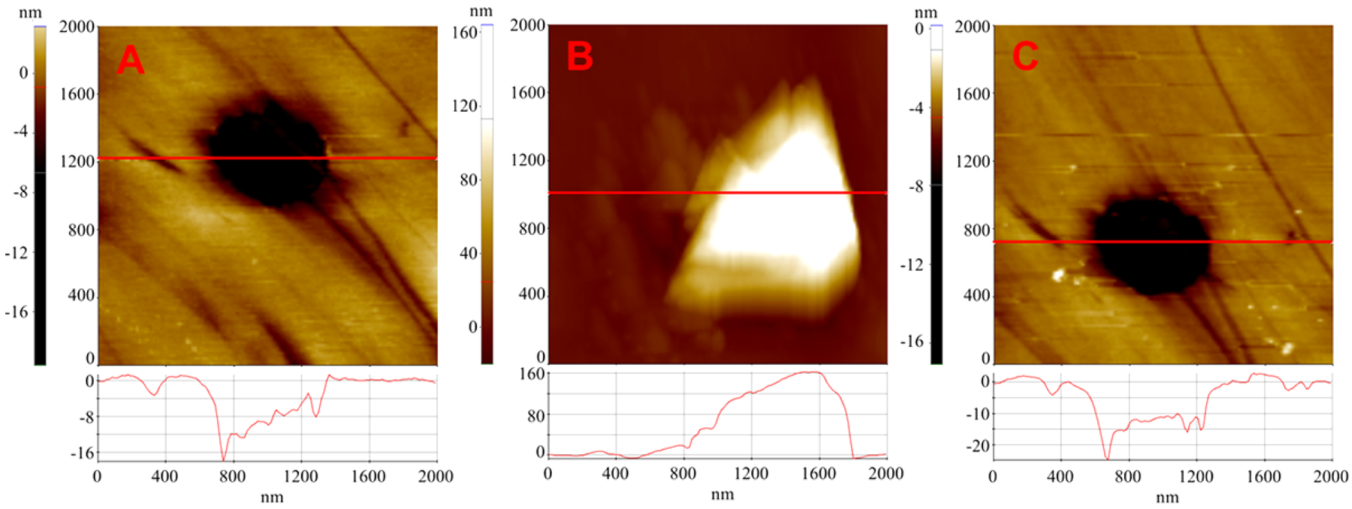

Figure 3. Noncontact AFM topography images of a polished Pt nanoelectrode before (A) and after (B) electrografting of a polymer film and after the film removal by plasma treatment (C).

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film was removed and both the smooth glass and Pt surface can be seen in Figure 3C. This result suggests the possibility of repeated experiments involving the formation of organic monolayers and thicker films at the nanoelectrode surface.

■ CONCLUSIONS

A plasma cleaner is a useful tool for nondestructive cleaning of nanoelectrodes. The AFM images and electrochemical measurements taken before and after cleaning suggest that the air plasma treatment is effective in removing impurities and organic films from the electrode surface. In this way, one can avoid mechanic polishing of a contaminated (or surface-modified) nanoelectrode, which is likely to change the electrode shape and size and increase the thickness of its insulating sheath. Because fabricating similar nanoelectrodes is not straightforward, the use of plasma cleaning can facilitate the replication of nanoelectrochemical experiments and improve their reproducibility.

The time required for the electrode cleaning depends on various factors, including the amount and nature of impurities on its surface. The completeness of the impurities (or organic film) removal can be confirmed by AFM imaging of the electrode surface. Additional cleaning may improve the electrode response (cf. parts D and F of Figure 1). Although a simple air plasma cleaner performed well in our experiments, it may be possible to attain more efficient surface cleaning and film removal by optimizing the protocol, including the gas composition, vacuum, and treatment time.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Cox, J. T.; Zhang, B. *Annu. Rev. Anal. Chem.* **2012**, *5*, 253. (b) Chen, S.; Liu, Y. *Phys. Chem. Chem. Phys.* **2014**, *16*, 635.
(2) Mirkin, M. V., Amemiya, S., Eds.; *Nanoelectrochemistry*; CRC Press: Boca Raton, FL, 2015.
(3) (a) Bard, A. J.; Fan, F.-R. F. *Acc. Chem. Res.* **1996**, *29*, 572. (b) Murray, R. W. *Chem. Rev.* **2008**, *108*, 2688. (c) Kleijn, S. E.; Lai, S. C.; Koper, M. T.; Unwin, P. R. *Angew. Chem., Int. Ed.* **2014**, *53*, 3558.
(4) Velmurugan, J.; Noel, J. M.; Nogala, W.; Mirkin, M. V. *Chem. Sci.* **2012**, *3*, 3307.
(5) Luo, L.; White, H. S. *Langmuir* **2013**, *29*, 11169.
(6) Wang, Y.; Velmurugan, J.; Mirkin, M. V. *Isr. J. Chem.* **2010**, *50*, 291.
(7) (a) Wang, Y.; Noel, J.-M.; Velmurugan, J.; Nogala, W.; Mirkin, M. V.; Lu, C.; Guille Collignon, M.; Lemaître, F.; Amatore, C. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 11534. (b) Actis, P.; Tokar, S.; Clausmeyer, J.; Babakinejad, B.; Mikhaleva, S.; Cornut, R.; Takahashi, Y.; Novak, P.; Shevchuck, A.; Dougan, J. A.; Kazarian, S. G.; Gorelkin, P.; Unwin, P. R.; Schuhmann, W.; Klenerman, D.; Sviderskaya, E.; Korchev, Y. *ACS Nano* **2014**, *8*, 875.
(8) (a) Sun, T.; Yu, Y.; Zacher, B. J.; Mirkin, M. V. *Angew. Chem., Int. Ed.* **2014**, *53*, 14120. (b) Amemiya, S. In *Electroanalytical Chemistry*; Bard, A. J., Zoski, C. G., Eds.; CRC Press: Boca Raton, FL, Vol. *26*, in press.
(9) Nioradze, N.; Chen, R.; Kim, J.; Shen, M.; Santhosh, P.; Amemiya, S. *Anal. Chem.* **2013**, *85*, 6198.
(10) Scherson, D. A.; Tolmachev, Y. V. *Electrochem. Solid State Lett.* **2010**, *13*, F1.
(11) Krügera, P.; Knesa, R.; Friedrich, J. *Surf. Coat. Technol.* **1999**, *112*, 240.
(12) Nogala, W.; Velmurugan, J.; Mirkin, M. V. *Anal. Chem.* **2012**, *84*, 5192.
(13) (a) Sun, P.; Mirkin, M. V. *Anal. Chem.* **2006**, *78*, 6526. (b) Sun, P.; Mirkin, M. V. *Anal. Chem.* **2007**, *79*, 5809.
(14) Bard, A. J. *J. Am. Chem. Soc.* **2010**, *132*, 7559.
(15) (a) Amphlett, J. L.; Denuault, G. *J. Phys. Chem. B* **1998**, *102*, 9946. (b) Shao, Y.; Mirkin, M. V. *J. Phys. Chem. B* **1998**, *102*, 9915.
(16) Ceccato, M.; Bousquet, A.; Hinge, M.; Pedersen, S. U.; Daasbjerg, K. *Chem. Mater.* **2011**, *23*, 1551.
(17) Belanger, D.; Pinson, J. *Chem. Soc. Rev.* **2011**, *40*, 3995.

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